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OXYGEN-GENERATING PROCESS OF A NEW "CHEMICAL"  
GAS-PROTECTIVE DEVICE

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OXYGEN—GENERATING PROCESS OF A NEW "CHEMICAL"  
GAS-PROTECTIVE DEVICEDr. -Eng. Albert Hloch  
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ABSTRACT: "Chemical" oxygen-generating devices, employing air regeneration by passage over alkali peroxides or decomposition of alkali chlorates are discussed in connection with their application in gas masks and other breathing apparatus.

"Chemical", oxygen-generating gas-protective devices, also known as "self-contained" or "recycle-type" devices, provide the wearer with an artificial oxygen atmosphere which is isolated from the surrounding air and is generated, during use, through chemical reactions taking place in the device itself. Efforts are being made to eliminate by this design principle the need for compressed oxygen, stored in high-pressure cylinders at 150 atm, and for related high-pressure lines and reducing valves, because of which oxygen-generating gas-protective devices of older design are so heavy and sensitive. Elimination of compressed oxygen would not only significantly reduce the weight of the device, but would also make it unnecessary to replace the empty oxygen cylinder. The need for replacing this cylinder makes it difficult to use such self-contained devices, particularly in certain areas and for certain uses, e.g., military applications. Because of the limited range of protection provided by filter devices—since the war (World War I) generally known as "gas masks"—efforts to simplify self-contained devices providing total protection are of practical interest. /732\*

The "chemical" oxygen-generating devices currently on the market, do not satisfy these requirements. The oxygen-generating substance in these devices is an alkali peroxide. The exhaled air is allowed to pass over the peroxide to remove the carbon dioxide and water vapor contained therein and, simultaneously, to generate oxygen. The air regenerated in this manner is then reused. Although this idea of a "chemical equivalent" of human lungs, first proposed by Bamberger and Böck (1), seemed very attractive, its realization proved to be very difficult for the following reasons: a) The heat given off by the reaction causes an excessive rise in temperature of the inhaled air (above 60°C); b) the expansion and sintering of granular alkali peroxide with progressive use results in increased resistance to air flow which exceeds the permissible limit (160 mm H<sub>2</sub>O); c) since the reaction of the peroxide with exhaled air is sufficiently rapid only at somewhat elevated temperatures, during a certain initial use period ("breathing induction" period, 2-5 min) the device does not produce the required amount of oxygen. Attempts have been made to eliminate these deficiencies by

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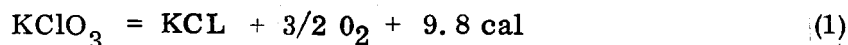
\*Numbers in the margin indicate pagination in the foreign text.

use of special peroxide processing techniques (addition of catalysts, introduction of 6% water); however, this approach is handicapped by the fact that the storage stability of the material is reduced by the water of hydration (2).

In contrast to this type of oxygen-generating apparatus, a new, recently introduced device \* generates oxygen by thermal decomposition of alkali chlorates. Here, the oxygen-forming process is independent of the breathing activity, in contrast to alkali peroxide-type devices in which this process is supposed to be regulated by the breathing. In the new device, as in equipment using compressed oxygen, carbon dioxide must be removed from the exhaled air by passing this air through cartridges containing granular caustic alkali. The new device is thus not based on the principle of simultaneous oxygen formation and carbon dioxide absorption in a single reaction. This indicates that, even after 25 years of development, it was not possible to apply this principle to gas-protective devices.

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A requirement for oxygen generation, in gas-protective devices, by thermal decomposition of chlorates according to the equation



is that it must be controllable. A sudden, non-regulated evolution of the total amount of oxygen required for a certain use period, as previously proposed for gas-protective devices, would make it necessary to store the oxygen. This could be achieved a) under conditions of practically no pressure, in gas-tight containers, e.g., rubber bags, which however, cannot be used in portable equipment, because of their excessive volume (a 300-~~1~~ capacity would be required for a 2-hour use period) or b) under pressure, in thick-walled, heavy containers, requiring pressure-reducing valves for removal of oxygen. Both these situations are to be avoided, however.

The oxygen supply must, therefore, be regulated so that the oxygen requirements of the wearer are satisfied both during light and heavy work conditions. According to specification guidelines for gas-protective devices used in mines, issued by the Prussian Commission for Mine Safety, such devices should be designed for an average oxygen consumption of 1.3 l/min, corresponding to a marching rate of 6 km/hr. In addition, they should provide enough oxygen for a peak consumption of 3 l/min for a minimum of 1 min and a maximum of 5 min. In the new device, oxygen generation from chlorate occurs at a rate of 2.5 l/min, which satisfies total oxygen requirements for medium and high work conditions. During peak activity, corresponding to an oxygen demand of 3 l/min, the wearer obtains additional oxygen from a breathing bag which is inserted into the breathing cycle, and has a capacity of 7 liters. This bag is filled with oxygen produced in increased amount during the starting period. Thus, during the period of peak activity lasting at the most 5 min, 2.5 l of oxygen is removed from the bag, with about 4 liters still remaining.

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\* Marketed under the trade mark "Naszogen", by Inhabad, G.m.b.H., Berlin.

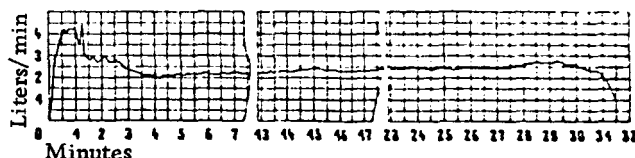


Figure 1. Oxygen evolution against time for a one-half hour "Naszogen" briquette.

A constant flow of oxygen, at a rate of 2.5 l/min, is obtained by restricting decomposition to a corresponding amount of chlorate per minute. This is achieved by use of a chlorate or perchlorate rod. The reaction is started at one end of the rod by an initial supply of heat. The heat liberated during decomposition according to equation [1] (this heat can be increased by the heat of oxidation from oxidizable additives, e.g., metals) then causes the decomposition of adjacent layers. In this manner, the reaction propagates along the entire length of the rod. However, the quantities of heat formed during the progressing exothermic reaction are additive and this causes a gradual increase in the rate of decomposition. As a result, constant oxygen evolution is impossible and, under certain conditions, the process may even become explosive. This possibility is eliminated by addition of substances which, while undergoing the exothermic main reaction, also undergo an endothermic change brought about by this exothermic reaction such as melting, vaporization, decomposition or endothermic reaction with other compounds. In this manner, it is possible to produce a regulated oxygen stream which is sufficiently constant for the purpose considered here (Fig. 1). It is even possible to increase or decrease the flow rate at will; for example, during the first 2-3 minutes after oxygen evolution is started by percussion, the oxygen rate may be raised up to 6 l/min to fill the breathing bag and to flush the apparatus with oxygen. Because of this, no "breathing induction" period is required as is the case with peroxide-based devices, the apparatus being immediately ready for use which is of paramount importance in nearly all cases.

To ensure propagation of the reaction, it is necessary to maintain a constant chlorate decomposition temperature (this temperature is reduced to about 300°C by use of catalysts). This is accomplished by suitable selection of the exothermic and endothermic-controlling additives and by proper arrangement of the insulating jackets. Tests at low temperatures (-42°C) have shown that cooling does not interrupt oxygen evolution; by contrast, the peroxide devices fail at temperatures slightly below 0°C. For this reason, the "Naszogen" process may be used also to supply oxygen to underwater diving equipment and high-altitude breathing devices for fliers.

The operation of such a gas-protective device, designed for a 1-hour use period, is illustrated in Fig. 2. The exhaled air passes through the right-hand corrugated tube and an exhaling valve into the carbon dioxide-adsorbing cartridge. The oxygen pronounced continuously in the "O<sub>2</sub> generator" at a rate of 2.5 l/min, passes through a ceramic candle filter where entrained dust particles (primarily KCl) are retained and enters the breathing cycle downstream from the exhaling valve; here it comes together with the exhaled air, and the resulting

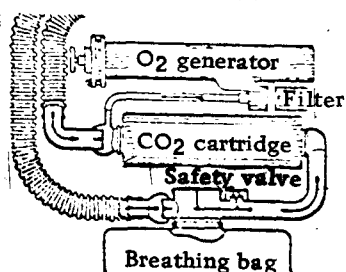


Figure 2. Schematic representation of a "Naszogen" gas-protective device.

mixture then passes through the carbon dioxide-adsorbing cartridge where contaminants, mainly consisting of 0.2 - 0.5%  $\text{CO}_2$ , are removed. The regenerated air

leaving the cartridge enters a breathing bag of approximately 7 l capacity which serves as a reservoir for the breathing air and for a certain amount of reserve oxygen for use during periods of peak activity. The air then passes through the inhaling valve and the left-hand corrugated tube and is inhaled by the user. Unused oxygen escapes through an automatic membrane-type safety valve actuated by a lever.

It is important that the temperature of the inhaled air be low. Absorption of contaminants from the exhaled air in the alkali cartridge generates about 126 cal at a marching rate of 7 km/hr; as a result, the air leaving the cartridge is heated as high as 120°C. Before this air reaches the user's mouth, this temperature must be reduced to below 50°C. In the case of "chemical", self-contained devices, this heat is augmented by that produced during oxygen generation. Devices using sodium peroxide generate, for example under the above-cited work conditions, more than 400 calories; as a result the breathing air is heated to such a high temperature that attempts to cool this air during its short travel to the mouth under fast breathing conditions have thus far encountered insuperable difficulties.

The heat given off during oxygen generation from chlorates amounts to only about 130 cal/hr and exerts only a minor effect on the breathing air. As regards the location of the heat sources, devices of this type differ substantially from those just described in that, in the peroxide devices, these sources are located in the breathing cycle itself, whereas in the chlorate devices they are outside this cycle. In other words, the inhaled air is heated only by the heat introduced with the oxygen (2.5 l/min). This heat amounts to only about 2 - 3 calories and is almost negligible compared to that given off during absorption of the contaminants from the exhaled air.

The principle considered ideal for self-contained equipment has not been adopted in this new device. This principle is based on the use of the carbon dioxide and moisture content of the exhaled air as a measure of oxygen demand, and as a means for controlling oxygen generation correspondingly. Neglecting the technical difficulties which preclude realization of such devices, the problem is incorrectly formulated from a physiological standpoint. Thus, for example, the increased amounts of carbon dioxide and water formed as a result of increased work produce an increased quantity of oxygen only after this quantity was needed by the body. In the continuing development of peroxide devices, this has been taken into account by partially hydrating the sodium peroxide. In this manner, oxygen evolution occurs also under the effect of heat and not only in dependence of the amount of carbon dioxide and water in the air.

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2. G. Stampe and E. Horn, Z. Angew. Chem. Vol. 42, p. 776, 1929.

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